STM JOURNALS

Omni Science:
A Multi-disciplinary Journal

https://journals.stmjournals.com/osmj/

ISSN: 2231-0398 (Online)
ISSN: 2347-9949 (Print)
Volume 14, Issue 3, 2024
September–December
DOI (Journal): 10.37591/OSMJ

Research OSMJ

Optimization of Reaction Parameters for Biodiesel (Methyl Ester) Synthesis Using Surface Response Methodology

P.O. Asipita[1,*], H.O. Haruna[2], M.M. Ambursa[3], I.G. Wawata[4], F.A. Atiku[5], J. Ibrahim[6], L.A. Musa[7]

Abstract

*The Polyoxo vanadate catalytic trans-esterification of waste cooking oil (WCO) was carried out by optimizing four reaction parameters which include: catalyst loading, methanol/oil ratio, temperature, and reaction time. These optimized parameters are 0.5 g, 0.8 g, and 1.2 g catalyst loading, 3:1, 6:1 and 9:1 methanol/oil ratio, 45°C, 60°C and 65°C reaction temperature, 45 min, 60 min and 90 min reaction time. The regression equation in the uncoded units of the optimization revealed that for every 1% increment in catalyst loading there tends to be a 15.64% increment of the biodiesel yield, more so 1% decrease in the interaction of methanol and time tends to increase the yield of the diesel by 0.0691% though under an ideal condition if there are no methanol/oil ratio, catalyst, methanol/oil * Time, 43.7 % is given for the unexplained parameter residual in the equation. A normal probability plot shows that, all the observations of % yield fit in the same line or trend. The Pareto chart of standardized shows that the catalyst loading has a high and strong effect on the biodiesel yield as it is the only parameter with such a standard effect of 1.492, the effect of methanol/oil interaction tends to follow the catalyst loading with a less standard effect of 1.0. The Contour plot of % yield vs Time, methanol/oil ratio reveals that at constant catalyst loading the interaction deepens when yield is above 50%. When the time is held constant, the Surface plot reveals the best output of the yield with catalyst loading of 0.8 g, methanol/oil ratio of 9:1, and 90 min reaction time. However, the R-squared value standard reports that about 34.52% of the parameters are explained by the yield which might be diagnostic for unusual observation on the yield with the value of 50.23% and 76.44% attributed by random chance. The biodiesel sample's FTIR measurement clearly verifies that waste oil was converted to biodiesel.*

***Author for Correspondence**
P.O. Asipita
E-mail: asipitapo@custech.edu.ng

[1–2]Research Scholar, Department of Science and Technology Education, Confluence University of Science and Technology, Osara, Nigeria
[3]Research Scholar, Department of Pure and Applied Chemistry, Kebbi State University of Science and Technology, Aliero, Nigeria
[4]Research Scholar, (Ph.D),Department of Industrial Chemistry, KIU Western Campus Bushenyi, Uganda, East Africa
[5]Research Scholar, (Ph.D.), School of Chemical & Process Engineering, University of Leeds, LS2 9JT, UK
[6–7]Research Scholar, Department of Chemistry, Confluence University of Science and Technology, Osara, Nigeria

Received Date: October 29, 2024
Accepted Date: November 01, 2024
Published Date: November 06, 2024

Citation: P.O. Asipita, H.O. Haruna, M.M. Ambursa, I.G. Wawata, F.A. Atiku, J. Ibrahim, L.A. Musa. Optimization of Reaction Parameters for Biodiesel (Methyl Ester) Synthesis Using Surface Response Methodology. OmniScience: A Multi-disciplinary Journal. 2024; 14(3): 20–28p.

Keywords: Biodiesel, catalyst, optimization, parameter, pollution, polyoxovanadate, transesterification

INTRODUCTION

Alternative sources of fuel from waste feedstock are of greater advantage due to the fact they do only provide an eco-friendly fuel but also help in waste disposal to further reduce pollution. Globally, the quest to produce alternative fuels other than fossil fuel has drawn the attention of so many researchers due rise in demand, price, and pollution caused by fossil fuels. This area of biodiesel production in recent research has sort to produce a more efficient biodiesel from feedstock which are of plant and animal origin without posing a threat to food security. Different kind of methods has been used for the production of biodiesel from oils gotten vegetable or triglycerides conversion. The direct use of triglycerides or vegetable oil, micro-emulsion, thermal cracking, and trans-esterification are the four main categories deployed.

The trans-esterification of high free fatty acid sources, such as animal fats, with alcohol, such as methanol (MeOH) or ethanol in the presence of an acid or base catalyst as a fatty acid methyl ester (FAME) or fatty acid ethyl esters (FAEE), or the trans-esterification reaction of edible or non-edible oil for the production of biodiesel [1].

Biofuels are mostly gotten from edible oil, fats, waste cooking oil, nonedible oil, and algae that are a product of the trans-esterification reaction of triglycerides with methanol. The most common component in biodiesel is Fatty acid methyl esters (FAMEs) because methanol used in the production process is more economically feasible and available than other alcohols [2]. During the esterification process, one mole of triglyceride (TAG) will produce 3 moles of Fatty acid alkyl esters (FAAEs) and 1 mole of glycerol in the presence of a suitable catalyst, monoglycerides (MAGs) and diglycerides (DAGs) are produced as intermediate products [3]. One molar excess of alcohol is usually supplied in trans-esterification reactions that are reversible to drive the mechanism toward the desired products. If methanol is used, the reaction mixture at the beginning is biphasic because methanol is sparingly soluble in triacylglycerol oils as shown [4].

About 100 million gallons of waste cooking oil is produced per day in the USA according to Energy Information Administration (EIA) in the United States (USA) estimation of which around 9 pounds of waste cooking oil are produced by one person per year [5]. The problems of disposal and contamination of resources from water and land have made waste cooking oils and fats management pose a great challenge [6]. While a portion of the waste oil is utilized in soap production, a majority of it is released into the environment, leading to pollution. Waste cooking oil (WCO) can be converted into biodiesel, which is a vital addition to the present energy system and helps reduce pollution [7].

This research employs waste edible oil feedstock (i.e., waste cooking oil) and optimizes the trans-esterification reaction parameters to reduce the expense, pollution, and hazard to food security associated with the manufacturing of biodiesel.

MATERIALS AND METHOD

Materials

The feedstock (Waste Cooking Oil) was obtained from a food vendor in Birnin Kebbi, Kebbi state, Nigeria. The waste oil is pretreated at room temperature by filtering to remove any inorganic residue and suspended matter. Conventional standard laboratory reagents, apparatus, and other equipment were also used. All the glassware required was soaked for 24 hours in dilute nitric acid and then rinsed in distilled water (H_2O) prior to the experiments.

Sample Pre-Treatment

After being heated to around 90°C for 60 minutes, the waste cooking oil (WCO) feedstock was filtered via filter paper to eliminate moisture and contaminants.

Determining the Physicochemical Properties of Waste Cooking Oil (WCO)

The following physicochemical parameters of waste cooking oil (WCO) were evaluated using AOCS procedures (AOCS, 1980; 2003) saponification value, acid value, free fatty acid value, and iodine value; ASTM D1298 (ASTM, 2002) was used to determine specific gravity.

Catalyst Preparation

0.8 g of ammonium metavanadate was dissolved in drops of distilled water which was afterwards mixed with 45 ml of methanol. The mixture was completely through continuous stirring. The stirred solution was dragged to pH 2 with a few drops of dilute and NH_4OH and HNO_3 solutions.

Reaction Parameter Optimization

A Response surface experimental (Box-Behken) design with 27 runs was designed using Minitab Statistical Software for four reactions parameters which include: Catalyst loading (g), Temperature (°C), Methanol/oil ratio, and Time (Min). Table 1 shows the range of values of the optimized parameter for the Trans-esterification reaction.

Table 1. Table showing the range of Optimization parameters.

Reaction Parameters	Lowest Value	Mid Value	Highest Value
Catalyst Loading (g)	0.5	0.8	1.2
Temperature (°C)	45	60	90
Methanol/oil ratio	3:1	6:1	9:1
Time (min)	45	60	90

Trans-Esterification Process

Exactly 5 ml of the pretreated oil was measured into a two-bottle neck round bottom flask which was fitted with a reflux condenser and heated at 60°C. A solution of promoted poly-oxo vanadate ions as catalyst with methanol was prepared through the measurement of a known amount of catalyst and a methanol volume calculated according to each experimental run. A magnetic stirrer was used to appropriately stir the mixture. The prepared catalyst and methanol were poured into the warm waste cooking oil. The reaction temperatures were varied for each experimental run, the number of catalysts used varied based on each experimental run, and the reaction time was in accordance with each experimental run. The resulting mixture in the two-bottle neck round bottom flask will be fitted on a magnetic hot plate which was subjected to heating at the temperature of the run with constant stirring using a magnetic bar for the run time as shown in Figure 1; the mixture was left overnight in a separating funnel after reaction time to settle as shown in Figure 2 for the different runs. The produced biodiesel appeared on the top layer in the funnel which will be separated while the two lower layers comprise glycerol and catalyst and were later separated using a centrifugation machine. The glycerol was used to calculate the percentage yield of the biodiesel using equation 1 below. The quantity of biodiesel (methyl ester) collected was dried to remove the water contents while the excess methanol was distilled [6].

Calculation: $\%\ \text{yield of biodiesel} = \frac{\text{Amount of transesterified oil}}{\text{Weight of glycerol}} \text{ x } 100$ Eqn. (1)

where

Amount of oil = weight of oil – weight of glycerol.

Figure 1. Trans-esterification experimental setup.

Figure 2. Trans-esterified Oil Separation Setup.

Biodiesel Characterization

The biodiesel produced was characterized using the Fourier-transform infrared (FTIR) spectroscopic method to confirm the transformation of the oil as a result of the trans-esterification reaction.

RESULT AND DISCUSSION

The Physicochemical Properties of Waste Cooking Oil Feedstock Result and Discussion

Table 2 shows the physicochemical properties of the feedstock (Waste Cooking Oil). At room temperature, the Waste Cooking Oil (WCO) is liquid and has a brownish color.

Table 2. Physico-chemical characteristics of the used cooking oil.

Parameters	**Value**
Color	Brownish
Specific Gravity (g)	0.93
State at room temperature	Liquid
Viscosity (mpas^{-1})	25.50
Density (g/cm^3)	0.91

Acid value (mg KOH/g)	0.66
Free fatty acid (%)	0.30
Saponification value (mg KOH/g)	181.9 ± 0.25
Iodine value (mg I/g)	105.48 ± 1.0

Each result's mean is determined in triplicate.

Specific Gravity

According to the investigation, the used cooking oil has a specific gravity of 0.93 g/cm^3, which falls within the acceptable range for most oils. This value of specific gravity influences the feasibility of utilizing waste cooking oil directly as fuel in diesel engines.

Acid Value

Table 1 presents the acid and free fatty acid values of the used oil, which are recorded as 0.66 mg KOH/g and 0.34%, respectively. As indicated by Leung and Guo (2006) [8], oils with higher acid values often result in the formation of soap when combined with acidic catalysts, leading to catalyst deactivation and reduced biodiesel yield. The significantly low acid and free fatty acid levels observed in the waste cooking oil demonstrate the effectiveness of the Polyoxovanadate (POV) catalyst for the trans-esterification process of the waste cooking oil [9].

Iodine Value

The waste cooking oil exhibits an Iodine value of 105.48 (Iodine mg/g), which falls within the acceptable limit defined by AOCS. This figure sheds light on the oil's degree of unsaturation and oxidative stability. However, it is worth noting that the value is below the threshold of 115 g/I$_2$ 100g typically set for dry oils [10].

Saponification Value

The saponification value of the leftover frying oil was 181.9 mg KOH/g, which falls within the limit prescribed by AOCS. This saponification value serves as an indicator of the oil's tendency to generate soap during the trans-esterification reaction, potentially leading to a decrease in the biodiesel yield [11, 12].

Result and Discussion of the Optimization of Biodiesel Production

Biodiesel Optimization

In the optimization, it was found that catalyst loading of 0.8 g, temperature of 60°C, methanol/oil ratio of 9:1, and time of 90 min were the reaction parameter combination that gave the highest yield of biodiesel of 76.44%.

Regression Equation in Uncoded Units of the Optimization

% Yield	=	43.7 + 15.64 Catalyst loading – 2.67 Methanol/oil ratio – 0.255 Time + 0.0691 Methanol/oil ratio * Time.

The regression equation reveilles that for every 1% increase in catalyst there tends to be a 15.64% increment of the biodiesel yield, more so a 1% decrease in the interaction of methanol and time tends to increase the yield of the diesel by 0.0691%.

All things being equal if there is no methanol/oil ratio, catalyst, methanol/oil * Time, 43.7% is given for the unexplained parameter residual in the equation. All in all, from the statistics catalyst tends to have more influence [13, 14].

Normal Probability Plot

From Figure 3 above, the normal probability plot shows that all the observations are not far from the trend (fitted) line, i.e., they are close to the trend line.

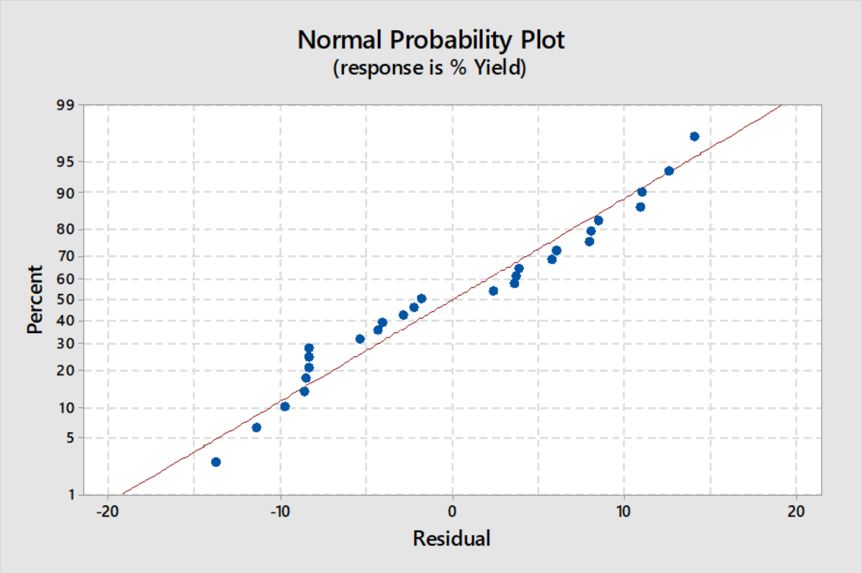

Figure 3. Normal probability plot (Response is % Yield).

Pareto Chart

From Figure 4, the Pareto plot reveals the standard effect of each of the parameters on the yield where the catalyst loading has a high and strong effect on the yield as the only parameter with such effect at a standard effect of 1.492. However, the effect of the interaction of methanol to oil ratio and time tends to follow the catalyst, though it has a lower standard effect of 1.0 and then followed by methanol and time alone. In actual effect, the catalyst is more effective on the yield.

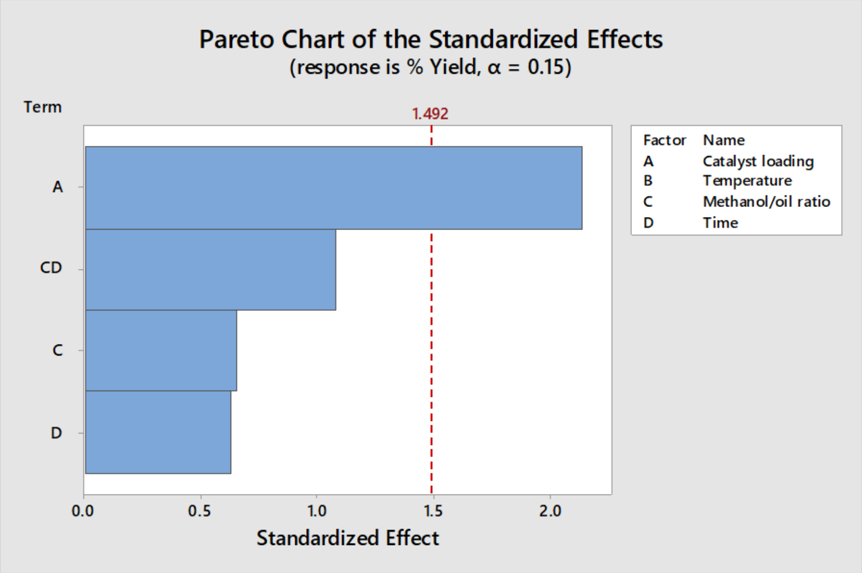

Figure 4. Pareto chart of the standard effect.

Contour Plot of % Yield vs Time, Methanol/Oil Ratio

From Figure 5, the interaction tends to be deeper when the yield is above 50% and the catalyst loading held constant.

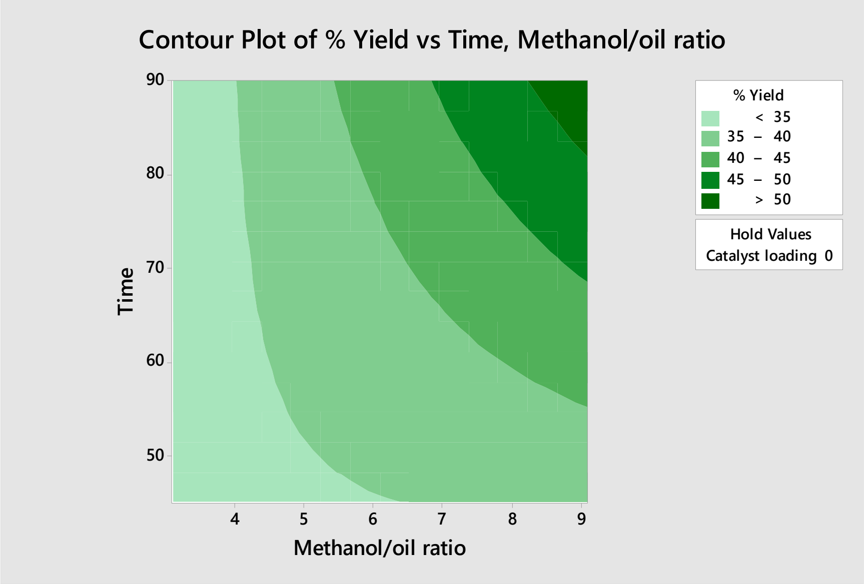

Figure 5. Contour plot of % yield vs time, methanol to oil ratio.

Surface Plot

From Figure 6, when time is held constant (T = 0) the surface plot reveals that the best output of the yield is at catalyst loading of 0.8 g and methanol to oil ratio of 9:1.

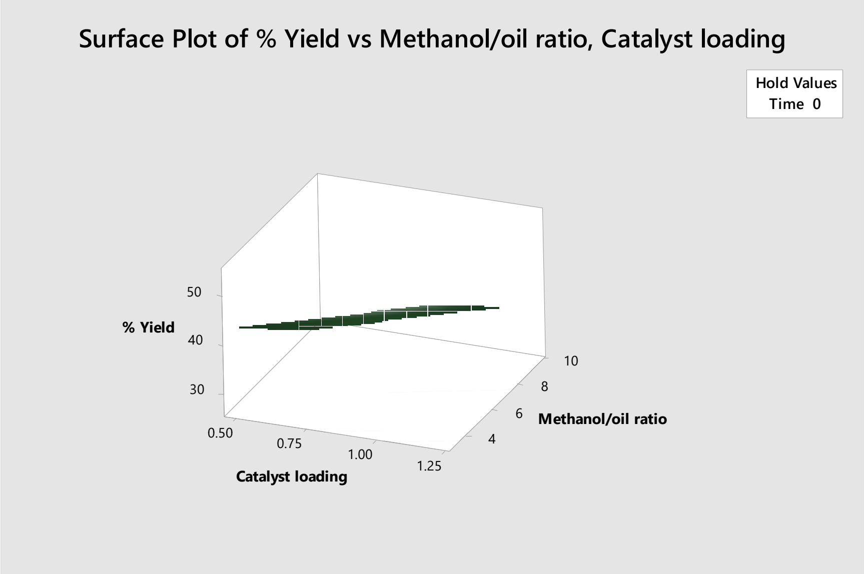

Figure 6. Surface plot of % yield vs methanol to oil ratio, catalyst loading.

Model Summary

From Table 3, the R-squared value standard reports that about 34.52% of the parameters are explained by the yield. However, this might tend to be diagnostic for unusual observation on the yield with the value of 50.23% and 76.44% attributed by random chance, i.e., a mistake outside control.

Table 3. Model Summary.

S	R-sq	R-sq (adj)	R-sq (pred)
8.94346	34.52%	22.61%	0.00%

Characterization of Biodiesel

FTIR Characterization of Biodiesel

The FT-IR spectra of the leftover cooking oil and the biodiesel made from it are shown in Figure 7 above. Characteristic peaks in the spectra include those at 2924 cm^{-1} and 2853 cm^{-1}, which correspond to the symmetric and antisymmetric stretching vibrations of C–H in the CH_2 and CH_3 groups, respectively. Another strong peak at 1743 cm^{-1} reveals the stretching vibration of carbonyl groups (C–O) present in the triglycerides of the waste cooking oil.

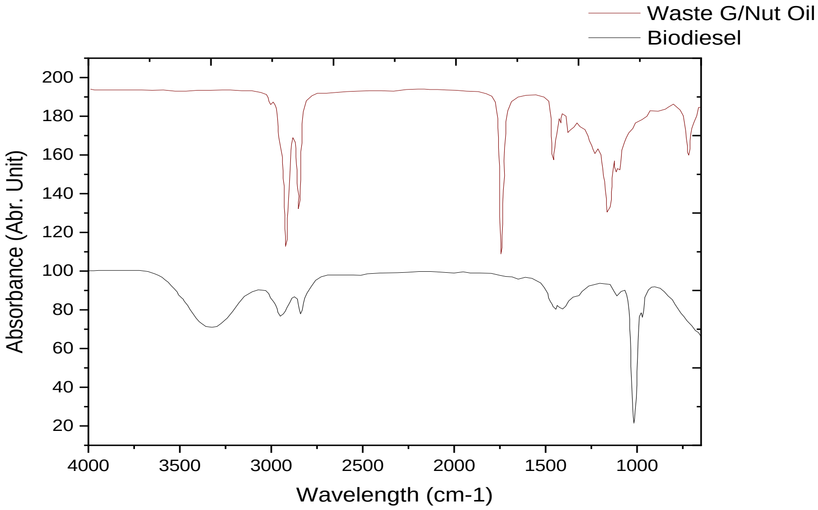

Figure 7. FT-IR analysis of Biodiesel and waste cooking oil. (Biodiesel in black, WCO in wine).

The peaks in the range of 1400–1200 cm^{-1} confirm the bending vibrations of CH_2 and CH_3 aliphatic groups in both the biodiesel and waste cooking oil. Additionally, HCH bending occurs at 1373 cm^{-1}, while CH_2 scissoring is observed at 1466 cm^{-1}.

The region between 1120–1090 cm^{-1} exhibits peaks corresponding to the ester stretching vibration (C–O), which is more pronounced in the biodiesel spectra. Furthermore, a peak at 1742 cm^{-1} confirms the stretching vibration of C=O in the esters, and peaks in the range of 1300–1000 cm^{-1} correspond to the stretching vibrations of C–O. Due to the presence of triglycerides and esters, the FT-IR spectra of the biodiesel and waste cooking oil show similarities.

However, slight differences were observed, such as the shift of peaks from 1743–876 cm^{-1} in the waste cooking oil to 1742–884 cm^{-1} in the biodiesel.

Notably, the disappearance of peaks at approximately 1543 cm^{-1} and 1198 cm^{-1} in the waste cooking oil spectrum, and the emergence of new peaks at 1430 cm^{-1} and 1024 cm^{-1} in the biodiesel spectrum, confirm the successful conversion of waste cooking oil into biodiesel. Nevertheless, a peak in the 3100–3500 cm^{-1} range indicates that the produced biodiesel may contain methanol and water traces, which can be removed using the refluxing and drying of silica gel.

CONCLUSIONS

In this research, Polyoxovanadate (POV) was successfully used for the trans-esterification of waste cooking oil to biodiesel. A yield of 76.44% was obtained for biodiesel with a catalyst loading of 0.8 g, using a 1:9 oil-to-methanol ratio, for 90 minutes at a temperature of 60°C. However, the R-squared value standard shows that about 34.52% of the parameters are explained by the yield. The regression equation shows that 43.7% is given for the unexplained parameter residual in the equation. From statistical study, the catalyst tends to have more influence.

REFERENCES

1. Gupta AR, Rathod VK. Waste cooking oil and waste chicken eggshells derived solid base catalyst for the biodiesel production: Optimization and kinetics. Waste Manag. 2018 Sep 1;79:169–78.

2. Vicente G, Martínez M, Aracil J. Optimization of integrated biodiesel production. Part I. A study of the biodiesel purity and yield. Bioresour Technol. 2007;98(9):1724–33. doi:10.1016/j.biortec.2006.7.024
3. Zhang P, Chen X, Leng Y, Dong Y, Jiang P, Fan M. Biodiesel production from palm oil and methanol via zeolite derived catalyst as a phase boundary catalyst: An optimization study by using response surface methodology. Fuel. 2020 Jul 15; 272:117680.
4. Dunn, RO. Effect of minor constituents on cold flow properties and performance of biodiesel. Prog Energy Combust Sci. 2009;35(6):481–9. doi:10.1016/j.pecs.2009.07.002
5. Patil PD, Gude VG, Reddy HK, Muppaneni T, Deng S. Biodiesel production from waste cooking oil using sulfuric acid and microwave irradiation processes. J Environ Protect. 2012 Jan 5;3(1):107–13.
6. Boakye P, Boakye P. Biodiesel production from selected non-edible feedstocks using unsupported potassium carbonate. M.Sc. Thesis, Kwame Nkrumah University of Science and Technology; 2013. Retrieved from: http://hdl.handle.net/123456789/5515
7. Sadaf S, Iqbal J, Ullah I, Bhatti HN, Nouren S, Nisar J, et al. Biodiesel production from waste cooking oil: an efficient technique to convert waste into biodiesel. Sustain Cities Soc. 2018;41:220–6.6.
8. Leung DYC, Guo Y. Transesterification of neat and used frying oil: optimization for biodiesel production. Fuel Process Technol. 2006;87(10):883–90.
9. Wawata IG, Ambursa MM, Asipita PO, Obaid FA, Babayemi W. Polyoxovanadate Catalyzed Synthesis of Biodiesel (Methyl Esters) from Waste Cooking Oil. KJSET. 2023;2(2):157–65. doi:10.59568/KJSET-2023-2-1-20
10. Abdulkareem AS, Uthman H, Afolabi AS, Awenebe OL. Extraction and optimization of oil from Moringa oleifera seed as an alternative feedstock for the production of biodiesel. Sustainable Growth Appl Renew Energy Sourc. 2011;244–68.
11. Cd AO. Cd 3-25. Official Method Saponification Value, Sampling and Analysis of Commercial Fats and Oils. Urbana (IL): The American Oil Chemists' Society; 2003.
12. Chavarria-Hernandez JC, Pacheco-Catalán DE. Predicting the kinematic viscosity of FAMEs and biodiesel: Empirical models. Fuel. 2014 May 15;124:212–20.
13. Huang Y, Li F, Bao G, Wang W, Wang H. Estimation of kinematic viscosity of biodiesel fuels from fatty acid methyl ester composition and temperature. J Chem Eng Data. 2020;65(5):2476–85.
14. Mostafa SS, El-Gendy NS. Evaluation of fuel properties for microalgae Spirulina platensis bio-diesel and its blends with Egyptian petro-diesel. Arab J Chem. 2017;10:S2040–5.